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ENGINEERING CHANGE NOTICE

Page 1 of 2

1. ECN No 617533

Proj. ECN

2. ECN Category (mark one) Supplemental [] Direct Revision [x] Change ECN [] Temporary [] Standby [] Supersedure [] Cancel/Void []	3. Originator's Name, Organization, MSIN, and Telephone No. C. J. Benar, 74610, H5-27, 372-1256	3a. USQ Required? [] Yes [X] No	4. Date 7/14/95
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12. Description of Change

Complete revision of document. Attachment A was deleted.

AUG 1995 RECEIVED ECNC

13a. Justification (mark one)

Criteria Change	[]	Design Improvement	[]	Environmental	[]	Facility Deactivation	[]
As-Found	[X]	Facilitate Const	[]	Const. Error/Omission	[]	Design Error/Omission	[]

13b. Justification Details

Changes were suggested to bring this document into conformance with current Data Quality Objectives guidelines.

14. Distribution (include name, MSIN, and no. of copies)

See attached distribution sheet.

RELEASE STAMP

OFFICIAL RELEASE BY WHC 2
DATE JUL 20 1995

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A-7900-013-1

ENGINEERING CHANGE NOTICE

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15. Design Verification Required	16. Cost Impact				17. Schedule Impact (days)	
	ENGINEERING		CONSTRUCTION			
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[X] No	Savings	[] $	Savings	[] $	Delay	[] N/A

18. Change Impact Review: Indicate the related documents (other than the engineering documents identified on Side 1) that will be affected by the change described in Block 12. Enter the affected document number in Block 19.

SDD/DD	[]	Seismic/Stress Analysis	[]	Tank Calibration Manual	[]
Functional Design Criteria	[]	Stress/Design Report	[]	Health Physics Procedure	[]
Operating Specification	[]	Interface Control Drawing	[]	Spares Multiple Unit Listing	[]
Criticality Specification	[]	Calibration Procedure	[]	Test Procedures/Specification	[]
Conceptual Design Report	[]	Installation Procedure	[]	Component Index	[]
Equipment Spec.	[]	Maintenance Procedure	[]	ASME Coded Item	[]
Const. Spec.	[]	Engineering Procedure	[]	Human Factor Consideration	[]
Procurement Spec.	[]	Operating Instruction	[]	Computer Software	[]
Vendor Information	[]	Operating Procedure	[]	Electric Circuit Schedule	[]
OM Manual	[]	Operational Safety Requirement	[]	ICRS Procedure	[]
FSAR/SAR	[]	IEFD Drawing	[]	Process Control Manual/Plan	[]
Safety Equipment List	[]	Cell Arrangement Drawing	[]	Process Flow Chart	[]
Radiation Work Permit	[]	Essential Material Specification	[]	Purchase Requisition	[]
Environmental Impact Statement	[]	Fac. Proc. Samp. Schedule	[]	Tickler File	[]
Environmental Report	[]	Inspection Plan	[]		[]
Environmental Permit	[]	Inventory Adjustment Request	[]		[]

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

Document Number/Revision	Document Number/Revision	Document Number Revision

20. Approvals

Signature		Date
OPERATIONS AND ENGINEERING		
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QA	
Safety	
Design	
Environ.	
Other	
DEPARTMENT OF ENERGY	
Signature or a Control Number that tracks the Approval Signature	
ADDITIONAL	

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RELEASE AUTHORIZATION

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This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

T.L. Ontiveros   July 14, 1995

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6. Author

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Signature

Organization/Charge Code 74610/N4A2K

7. Abstract

This document represents the application of the Data Quality Objectives (DQO) process to the Flammable Gas Tank Wasty Issue at the Hanford Site. The product of this effort is a list of data required from tank core sample analysis to support resolution of this issue.

8. RELEASE STAMP

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WHC-SD-WM-DQO-004	

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FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES PROCESS

July 1995

N. G. McDuffie

Prepared by
Westinghouse Hanford Company
Richland, Washington

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FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES PROCESS

ABSTRACT

A Data Quality Objectives process was applied to the Flammable Gas Tank Safety Issue at the Hanford Site to define data requirements for the analysis of core samples from the flammable gas tanks. Information from core samples is required for development of mitigation methods, to support tank behavior models needed for making safety analyses, and to support evaluations of chemical mechanisms for gas production and release. Results from these evaluations will be used to support the basis for making decisions on mitigation and safe storage. Research and development studies in support of these decisions will be documented by separate test plans. These test plans will be submitted along with the applicable Data Quality Objectives for allocation of material from the core samples. Where applicable, historical data will be used so that the number of analyses can be minimized. The Data Quality Objectives will be reviewed routinely to optimize the sampling and analysis processes.

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FLAMMABLE GAS TANK SAFETY PROGRAM: DATA REQUIREMENTS FOR CORE SAMPLE ANALYSIS DEVELOPED THROUGH THE DATA QUALITY OBJECTIVES PROCESS

1.0 INTRODUCTION

The release of flammable gases into the dome space of Tank 241-SY-101 (101-SY) and other waste tanks at the Hanford Site is a top priority safety issue. Periodic releases of these gases has resulted, in a few instances, in concentrations above the lower flammability limit (LFL) for hydrogen and other contained fuels. Such venting of gases is expected to keep recurring until some form of mitigation or retrieval action is taken.

Insufficient knowledge has been obtained about the processes occurring within the waste that generate, retain, and release the gases. Collecting information about the basic chemical and physical properties of the waste is one of the main steps needed to gain knowledge about the behavior of the waste so that effective mitigation methods can be developed and implemented. In addition, information obtained from laboratory and modeling activities will help to support the basis for making decisions about the magnitude of the safety issue and for solving problems found in the process.

As an understanding of the behavior of the waste is developed, various mitigation methods can be devised to maintain the tanks in a safe condition. These mitigation methods may involve mechanical processes, chemical treatment, or a combination of both. A mixer pump has been installed in Tank 101-SY to mitigate the flammable gas safety issue in that tank. Thorough reviews of successes for this operation will allow projections for possible pump applications in the other double-shell tanks on the Flammable Gas Watch List. These projections can include evaluations of direct mitigation without complete characterization, a process that could save the costs of detailed characterization. If any of the single-shell tanks are found to require mitigation, methods other than use of mixer pumps will be needed. Closure of the safety issue hinges on prevention of flammable gas burns, including burns under crusts, in plumes, and in ventilation systems and tank domes. Analyses provided for in this Data Quality Objectives (DQO) document give concentrations of toxic substances and radioactive materials for use in hazard assessments needed for safety analyses of the safety issues. This DQO document does not in itself provide for closure.

1.1 SCOPE

This DQO document was prepared for the Flammable Gas Tank Safety Program. The scope of this activity was to summarize the analytical needs for core sampling activities of the Flammable Gas Watch List tanks. Data from the core samples are needed to provide an understanding of the tank contents so that: (1) insight may be obtained on the mechanisms for gas generation, retention and release, (2) models of the waste behavior can be developed to support safety analysis and development of mitigation methods, (3) compositions of simulants for waste studies can be developed, and (4) modeling of the release of gases, and subsequent potential for ignition in the dome space, can be done to support hazard analyses. Special tests on the waste samples will be needed to evaluate gas generation, gas solubility, and the effects of heating and dilution on waste behavior. Test plans will be prepared for these activities. These test plans will incorporate statements, and justifications, of requirements for samples of tank core material over and above the requirements for laboratory analysis supporting this and other DQO. The product for this core sampling DQO is a list of data requirements. As an understanding is developed, it may be possible to specify decisions that can be made on the basis of core sample results. Once this is done, this DQO document will be revised to incorporate the requisite decisions.

Data of various types are required to evaluate safety issues arising from the presence of flammable gas mixtures in Hanford Site tanks, as well as to support mitigation of hazards disclosed through such evaluations. The primary categories of applicable data are as follows:

1. Physical operating data including in-tank temperature histories, dome pressure data, ventilation flow rates, surface levels, and other data, including video recordings of surface appearances and changes, obtained from specific tanks or groups of tanks.

2. Continuous or repetitive gas analyses obtained from continuous or intermittent gas monitoring systems on tank dome contents, individual tank ventilation exhausts, or tank group exhaust systems.

3. Laboratory gas analyses on grab samples from tank dome spaces, individual tank exhausts, or tank group exhaust systems.

4. Laboratory analyses of auger samples of crust or upper solids.

5. Laboratory analyses of waste samples obtained by push-mode or rotary-mode core sampling procedures, or even by the so-called "bottle-on-string" method.

6. Data obtained from in-tank test procedures (viscosity, yield strength, gas content, differential pressures, sound velocity and attenuation, penetrability, compressibility, and others that may be instituted).

7. Retained gas content and composition obtained from procedures involving a retained-gas sampler now under development.

The DQO for the Flammable Gas Watch List tank waste characterization are described in this presentation. The current document is not meant to contain a critical evaluation of data quality requirements for items 1, 2, 3, 4, 6, or 7, above. Item 4 is covered by a separate document (Johnson 1994), which was prepared separately in order to have it finished in time for the auger sampling of Tank 241-SY-103.

1.2 BACKGROUND

Major expectations of participants in the DQO development exercise were to accomplish the following tasks:

- Identify methods beyond the standard safety-screening (Babad 1994) suite that will address the safety problem(s).
- Determine what "level of quality" is needed for each analysis or parameter, including newly developing tests.
- Focus especially on data quality and data requirements for characterization.
- Ensure that data users are aware of laboratory and field measurement capabilities and that data users' requirements are well justified, sufficient, quantitative, and achievable.
- Focus on practical and useful analyses needed for specified purposes, using historical data when applicable.
- Generate a sampling and analysis plan that meets the needs of data users (by providing input to the specific Tank Characterization Plans, which will give the detailed plan).

This document provides the data requirements that evolved over the course of a number of meetings held from December 1993 through April 1994. The DQO planning team fully expects the data requirements and DQO to evolve over time. This approach is consistent with the Tank Waste Remediation System DQO Strategy (Babad et al. 1994) which states, "The identification of data requirements is intended to be an ongoing effort aimed at accommodating gains in information from any source, rather than a one-time data requirements identification activity." Core sampling of the waste will provide supporting data for the Flammable Gas Waste Tank Program decision processes, by providing a better understanding of the mechanisms behind gas releases, periodic, aperiodic, and steady state. A better understanding of gas release events may lead to modifications to the data requirements, which may be either more, or less, exacting than those currently accepted.

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2.0 THE FLAMMABLE GAS SAFETY ISSUE

Hydrogen gas is produced by radiolysis in most containers of radioactive solutions in water, so there are always concerns about accumulation of hydrogen, a very flammable gas, in vapor spaces of vessels of reactors, fuel storage systems, and radioactive waste storage tanks. These are concerns that are taken into account in designing related ventilation, exhaust, and purge systems for such equipment. The primary safety issue for the program is that related to episodic gas release events, noted especially in Tank 101-SY. The Hanford Flammable Gas Waste Tank Safety Program also is mandated to study older storage tanks to ensure that unsafe flammable gas concentrations do not accumulate. In addition to Tank 101-SY, the Flammable Gas Watch List contains 24 other tanks that either exhibit episodic gas releases like those in 101-SY, but to a lesser extent, or are considered likely to exhibit such releases. In all of the tanks generating flammable gases, some baseline steady-state or quasi-steady-state concentration of flammable gases will be present. This concentration can be high enough to be of concern especially in the passively-ventilated single-shell tanks. Its presence can exacerbate the effects of episodic releases. A number of the single-shell tanks have been showing level increases that are probably indicative of gas accumulation. Even those that have not shown such increases could be accumulating soluble gas (especially ammonia) or accumulating gas, but having the volume increase offset by leakage of liquid from the tank. Studies relating effects of barometric pressure changes on tank surface levels are in progress to evaluate volumes of stored gases. In situ measurement methods, as well as methods for obtaining samples without loss of retained gas (the Retained Gas Sampler) are under development.

2.1 BASIS FOR WATCH LIST

The Flammable Gas Tank Watch List was initially made up to include Tank 101-SY and any tanks containing materials related to contents of Tank 101-SY or tanks that exhibited slurry growth, episodic level drops, or pressure bumps. On this basis, the list is chosen conservatively, since Tank 101-SY, whose episodic activity is greater than that of any other tank, has exceeded lower flammability limits in the ventilation system in only a few events of very short duration. Another, more general, concern is that many tanks are producing smaller releases of gas containing fuel components mixed with the oxidizer, nitrous oxide. The released volume of gas would be flammable, and would be expected to ignite if a spark source were present in the same space. The probability of such ignition in a closed tank is considered to be very low, but possibly not incredible. Scenarios involving such processes are now under study. Outcomes of these studies could affect subsequent revisions of the Flammable Gas Watch List and related DQO. Also, as noted above, the general concern about accumulations of flammable gas mixtures in dome spaces and ventilation systems of tanks can lead to establishment of requirements for active ventilation of tanks now only passively ventilated. A separate process specification document is being prepared for gas monitoring activities (Sherwood 1995). In addition, the general safety screening process could lead to placement of more tanks on the Flammable Gas Watch List. In a current Flammable Gas Program activity, Pacific Northwest Laboratory (PNL) and Westinghouse Hanford Company (WHC) investigators are studying implications of effects of barometric pressure increases in lowering of surface levels of Hanford Site waste tanks. Initial studies indicate that a number of tanks not now on the Flammable Gas Watch List may be showing evidence of appreciable volumes of trapped gases. This study could lead to placement of more tanks on the Watch List.

2.2 CHEMISTRY OF GAS GENERATION

Gas generation chemistry of Hanford Site waste material has been studied at WHC (and its predecessor Hanford Site contractors/managers), Argonne National Laboratories, Georgia Institute of Technology, and PNL as well as other laboratories, to a lesser extent. Studies with simulant mixtures show that it is possible to produce flammable gas mixtures even without the presence of radiation. Radiolytic production of hydrogen is aided by the presence of organics and hindered by nitrite and nitrate ions. Chemical degradation of organics to produce hydrogen requires basic conditions (high hydroxide ion concentration), as well as the presence of aluminate in some form. To a large degree ammonia and nitrous oxide are produced by reduction of nitrite ion in the presence of organic compounds. The relative contribution of purely chemical production of gases as compared to radiolytic production has not yet been determined. Laboratory studies confirm the production of lesser amounts of methane (and some CO), especially at elevated temperatures. Furthermore, chemical and radiolytic chemical studies indicate that organic compounds such as some of the complexants are active in producing gases while more refractory organics, especially formate and oxalate (formic acid and oxalic acid anions) are not effective hydrogen producers under tank conditions. A general conclusion is that in Hanford Site radioactive wastes containing active organics, aluminum and nitrite the potential exists for production of flammable mixtures of hydrogen, ammonia, and nitrous oxide, along with low concentrations of methane and carbon monoxide.

Historically, the tanks considered primary flammable gas safety issue tanks have been those that contain complexant concentrate, double-shell slurry, or double-shell slurry feed, all process streams originally containing relatively high concentrations of organic compounds and relatively concentrated in salts to give combined (solids plus liquids) specific gravities over about 1.4.

2.3 PHYSICS AND PHYSICAL CHEMISTRY OF GAS RETENTION

The physics of gas retention and gas release is not completely understood; however, it is known that the relative densities of solid and liquid phases, as well as shear strength of gas-retaining layers are important factors determining the relative amount of gas retained before gas release can occur. Viscosities of the fluids and slurries are also of importance in the computer models used to simulate rollover activities of the tanks. The actual mode of attachment or trapping of gas in the slurries has not yet been ascertained. Current research is directed toward a better understanding of the physics of gas retention. Also, because sampling and sample handling affect rheological measurements, efforts are directed toward in situ measurements of viscosity and shear strength. Additionally, in situ measurements of gas content of tank layers are to be attempted under the Mitigation Program.

2.4 CURRENT UNDERSTANDING OF COMPOSITION OF RELEASED GAS

The current understanding of composition of gas released in gas release events is obtained from studies on Tank 101-SY. This tank is highly instrumented for monitoring of results of flammability mitigation activities, i.e., mixing with a pump. However, some uncertainty still exists regarding exact composition of the gas from gas release events, because a major component, nitrogen, has only been measured in a few prior grab samples during gas releases. The composition of the gas is variable. Two of the vapor components, ammonia and nitrous oxide, are appreciably soluble. Their release from solution, as well as release of water vapor, will depend on mass transport rate limitations. Ranges of gas compositions are summarized in Table 1. The major flammability concerns for Tank 101-SY and for the plume-burn issues are for the gases released during the Gas Release Events (GREs, Table 1A). For passively ventilated tanks, the baseline, or steady-state, releases are of concern, in addition to any possible episodic releases of trapped or dissolved gases. Examination of the information therein indicates that ammonia, not hydrogen, is the major flammable gas released from Tank 101-SY if the gas release event cycle time is as high as 180 days (see Table 1B). However, most of the ammonia is released in the periods between gas release events, when it is diluted by air from the ventilation flow. The LFL for ammonia in air is higher than it is for hydrogen in air (8 vol% for ammonia compared to 3.5 to 4 vol% for hydrogen). These values are modified by presence of nitrous oxide and by temperature and pressure. Detailed developments will be included in documents generated by the Accelerated Safety Assessment team (Van Vleet 1995).

Table 1. Tank 101-SY Released Gas Compositions.

A. Gas release events, released gas, dry basis, 2.83 E+2 to 3.68 E+2 m^3 (10,000 to 13,000 stdft^3) release		
Component	Content, volume %	Ratio: component/hydrogen
H_2	30-35	1.0
N_2O	25-30	0.7-1.3, av. ~0.8
N_2	20-25	0.6-0.8
NH_3	12-18	0.3-0.6
CH_4	≤1	≤0.03
Note: Water vapor (H_2O) content is about 4 volume %.		

B. Baseline between GREs, contents in 2.60 E-1 m^3/sec (550 ft^3/min) exhaust air flow			
Component	Content, p/M vol.	Average ratio to hydrogen	Approx. m^3/d (ft^3/d)
H_2	10-18, av. ~18	1.0	4.2 E-1 (15)
N_2O	12-40, av. ~22	~1.2	5.1 E-1 (18)
NH_3	40-100, av. ~40	~2.2	9.3 E-1 (33)

Notes: Methane (CH_4) not measurable above ambient air concentration levels. Nitrous oxide (N_2O) and ammonia (NH_3) concentrations reach the higher bounds during barometric pressure lows. Total releases (not including amount released in gas release event) during a 180-day period would be: H_2, 7.65 E+1 m^3 (2,700 stdft^3); N_2O, 9.06 E+1 m^3 (3,200 stdft^3); and NH_3, 1.67 E+2 m^3 (5,900 stdft^3).

2.5 THE CURRENT FLAMMABLE GAS SAFETY PROGRAM WATCH LIST

The current Flammable Gas Safety Program watch list contains the following tanks:

241-A-101
241-AN-103, 104, 105
241-AW-101
241-AX-101, 103
241-S-102, 111, 112
241-SX-101, 102, 103, 104, 105, 106, 109
241-SY-101, 103
241-T-110
241-U-103, 105, 107, 108, 109.

This list is subject to upgrading, especially during the current safety screening campaign. Vigilance should be maintained to respond to any changes in operations or any new developments in any of the waste tanks that indicate possible flammable gas implications. For example, tanks with high radionuclide contents should be monitored to evaluate flammable gas production. Process and transfer tanks (including the double-contained receiving tanks (DCRTs) are all prone to some buildup of flammable gas. The current DQO should provide guidance in developing logical sequences for evaluation of situations involving waste storage tanks not contained in the Watch List. As mentioned in Section 2.1, the results of safety screening activities might result in the addition of tanks to the Watch List.

2.6 OVERLAPPING WASTE TANK SAFETY PROGRAM ISSUES

Several of the Hanford Site waste tanks are covered by safety concerns under more than one specific program. The flammable gas watch list tanks that are covered by the Organic Safety Program in addition the Flammable Gas Tank Safety Program are as follows:

241-A-101
241-S-102
241-S-111
241-SX-103
241-U-103
241-U-105
241-U-107.

Safety screening may establish more overlapping concerns. For tanks covered by more than one safety concern, mutually acceptable data requirements must be established. Data quality objectives reports have been issued for the ferrocyanide (Buck et al. 1993), high-heat (Wang et al. 1994), and tank vapor issue (Osborne et al. 1994) safety issues, as well as for safety screening all tanks (Babad 1994). Tank 101-SY releases concentrations of ammonia and nitrous oxide far above limits deemed safe for unprotected workers. Other flammable gas watch list tanks are likely to do the same; thus there is certainly concern for toxic vapor released from the tanks. This must be taken into account for any safety assessments and work controls developed for work in, upon, and around the tanks. Within the Tank Vapor Issue Program, evaluations of flammability are made, as in studies of Tank C-103, and results are shared with the Flammable Gas Program.

2.7 RELATIONSHIP OF UNREVIEWED SAFETY QUESTIONS TO DATA QUALITY OBJECTIVES

An Unreviewed Safety Question (USQ) was declared in March 1990 (Daugherty 1990) with the issuance of an Unusual Occurrence Report (UOR). The report stated, in part, "Recent Westinghouse reviews of the tank vapor space flammability identified that the gas under the crust is potentially flammable because nitrous oxide N_2O and hydrogen can create flammable mixtures. This is considered an Unreviewed Safety Question." The existing Safety Analysis Report at that time did include the issue of hydrogen generation but did not specifically consider the hazard of a flammable mixture of hydrogen and nitrous oxide within the waste. Later, in May, the U.S. Department of Energy (DOE) issued a letter (Lawrence 1990), per the requirements of DOE Order 5480.5, that stated "DOE-RL has determined that the matter of hydrogen and nitrous oxide evolution within the material in certain waste tanks and subsequent hypothetical hydrogen ignition is an unreviewed safety question." The references to this letter provided identification of the tanks of concern.

Thus, the USQ was generated initially by a concern over the simultaneous generation of fuel (hydrogen) and an oxidizer (nitrous oxide). However, the extensive analytical and experimental work conducted for Tank 101-SY also have shown the need to consider other flammable gases such as ammonia and methane.

Closure of the USQ requires the following steps: (1) analyze the hazards, (2) implement work controls, (3) update the safety basis, (4) close the UOR, and (5) obtain DOE approval. The primary information needed for this process is knowledge of the amount and composition of the gas mixture that is (or can be) released into the dome space of a given tank. Modeling and judgement, based on experience and comparison of historical behaviors of tanks, provide further input concerning frequency, initiating factors, speed of gas release, etc., for bounding possibilities of gas releases, both steady-state and episodic. This information is then used to determine if there is a potential for ignition of the gas mixture.

Resolution of the USQ does not mean that the basic safety issue has been closed. Closure of the safety issue requires placing a tank in a safe condition by enhancing monitoring and operational controls, or by mitigating the existing situation, or maybe even by remedial actions involving waste treatment. Thus, closure of the safety issue is facilitated with in-depth knowledge of the waste. At the present time, the only Flammable Gas Watch List tank that has been characterized sufficiently to close the USQ is 101-SY. Even for Tank 101-SY, efforts are still underway to understand the properties related to gas generation, retention and release. The other double shell tanks on the Flammable Gas Watch List do exhibit episodic gas releases, but there is little information on the nature of the waste in the current situation. This DQO provides the data requirements for the items that need to be analyzed on Flammable Gas Watch List tank core segments (see Section 5.0) so that appropriate mitigation methods can be developed to address the basic problems of gas generation, retention and release.

2.8 MITIGATION REQUIREMENTS

Mitigation of flammable gas safety hazards may be achieved by a rather wide range of alternative actions, depending on the nature and grade of risk. Some of the types of mitigation possibilities and their related data requirements have been presented in reports for the Flammable Gas Mitigation Program (Ashby et al. 1992, Babad et al. 1992, Lentsch 1992). As indicated in these reports, the mitigation concepts involve either physical or chemical treatments. Each of these mitigation possibilities has its own set of data requirements, some exclusive, and others very general. The general data requirements covered by the current characterization effort are not meant to address all possible alternatives for mitigation. Obviously it is not advisable to obtain data for all of the conceivable modes of mitigation for the tanks, and especially for those that do not require mitigation. Ultimately all of the contents of all tanks will be retrieved for final disposal.

2.9 SUPPORTING OPERATIONAL DATA

Other operating data, historical and current, not covered in the present data quality objectives exercise, may be used in supporting safety analyses of flammable gas watch list tanks. Some of these (provided here for information only) are as follows:

- Tank ventilation flow rates (for actively ventilated tanks)
- Tank annulus ventilation flow rate where available
- Temperatures in tank contents (and resultant temperature profiles)
- Pressures in tank (generally gauge pressures) dome space
- Tank breathing rate (for passively ventilated tanks)
- Barometric pressure

- Temperatures of incoming ventilation air streams, dome spaces, exhaust, etc.
- Ambient air temperature, humidity, wind velocity and direction
- Surface level of waste in tank
- Liquid observation well liquid height or depth (single-shell tanks)
- Annulus, tank concrete temperatures
- Water content or relative humidity of tank exhaust
- Surface characteristics as indicated by in-tank visualization with video cameras installed in tanks.

2.10 USER GROUPS FOR FLAMMABLE GAS WASTE TANK DATA

Currently the primary user groups for the flammable gas waste tank data are as follows:

U.S. Department of Energy

Westinghouse Hanford Company
- Flammable Gas Safety Program, Tank Waste Remediation System
- Technical Data Analysts (with Numerical Applications, Inc.)
- Computer Modelers
- Safety Analysts
- Design Engineers

Pacific Northwest Laboratory
- Computer modelers
- Physical modelers
- Data Analysts
- Chemical Groups studying properties and reactions (with assistance from several university scientists)

Georgia Institute of Technology
- Chemistry Department group studying reactions of simulants

Los Alamos National Laboratory
- Safety Analysts
- Scientists studying mitigation processes
- Physical model developers.

2.11 QUESTIONS FOR RESOLVING THE PROBLEM

Data obtained from the flammable gas waste tanks will be used to answer the following questions in regard to the flammability problem:

1. Do the tanks present a real flammability problem (primary question)?

2. What is the composition of the slurry gas?

3. How much slurry growth is related to gas entrapment?

4. Is the level of gas evolution sufficient to cause a radiation or toxic release above risk acceptance guidelines (with or without ignition) during storage and normal tank operations or possible accident?

5. If the answer to Question (1) is affirmative, How can the situation be corrected? What control or mitigation actions are dictated?

It should be noted that this DQO does not directly address the data needed for the above questions, although the goal is to use tank data to aid in predictive modeling to answer such questions; a separate document (Sherwood 1995) is being prepared for gas monitoring of the tanks.

Secondary questions related to this DQO are:

6. What conditions are responsible for producing the flammable gas species? Can they be controlled; if so, how?

7. What conditions cause gas retention and subsequent episodic gas release? Can they be controlled; if so, how?

8. What would be the onsite and offsite radiation and toxic chemical dose consequences from a postulated gas burn or non-burn release (as determined through processes outlined in the Accelerated Safety Assessment [Van Vleet 1995], using data specified in this DQO document)?

9. What conditions are to be avoided in filling new waste tanks to prevent flammable gas problems from developing?

10. Are there follow-up data requirements?

2.12 SUPPORTING ANALYTICAL DATA

Chemical and physical characterization analyses of these core samples are deemed very important in the continuing efforts to understand the flammable gas generation, retention, and release issues related to the secondary questions listed in Section 2.11. These data will provide valuable input to the models being used to predict tank behavior and for verification of the laboratory work on waste simulants. Other input will be obtained from gas monitoring (Sherwood 1995). Successful modeling can hopefully obviate the need for complete characterization of every tank and, in addition, provide for prediction of future bounds of gas production and release activities.

A related effort is the activity directed to development of a retained gas sampling device and procedure for its use. Successful use of this device should provide knowledge of contents of volatile components retained in tank contents, both in restrained bubbles and in solution or at interfaces. When success is attained, suitability of the device for use in primary safety decisions can be evaluated. The use will be to provide basic data to predict compositions of tank headspace contents that could be produced under plausible mechanisms for release of retained gas. The decision rules are not expected to be changed to any great extent as a consequence of the related studies. However, this further evaluation will provide for firmer risk assessments for those tanks that have exhibited slurry growth without gas release and for tanks that may have stored large amounts of dissolved gas (especially ammonia), for possible mass-transfer release upon tank mixing. An analysis of potential error in measurements and related error propagation can be performed after trials of the experimental retained gas device(s).

3.0 DECISIONS TO BE MADE

As indicated at the beginning of this document, core sample data are needed to understand the chemical and physical processes occurring within the waste. As discussed in Section 2.11, there are questions that need to be answered.

- What conditions cause retention and subsequent release of the gas?
- What is the mechanism for gas generation?
- What situations are to be avoided in future operations so as not to create another "flammable gas tank?"
- What are the source terms for radiological and toxicological dose consequence calculations?

Characterization of the waste is needed in order to answer these questions. Closure of the flammable gas safety issue will require answers to these questions. At this time much information needs to be gathered in order to understand the processes occurring within the waste. This information will be used to develop future decisions for mitigation of the safety issue and for safe storage of the waste. In addition, the data provide key parameters for the models that have been developed for describing the behavior of the tank. Results of the modeling efforts have been required for the various safety analyses.

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4.0 INPUTS TO THE FLAMMABLE GAS DECISION PROCESS

As a result of the meetings summarized in Appendix A and based on the experience obtained with Tank 101-SY there are a number of analyses needed to answer the questions listed in Section 3.0.

For an understanding of gas retention and release:

- Stratum identification and description
- Density of bulk samples, liquid phase and settled solids
- Rheological properties(viscosity and shear strength)
- Solids content and settling rate
- Solubility of solids.

For an understanding of gas generation:

- Chemical composition of the waste
  - Analyses for major anions (including carbonate), cations, and water.
  - Total organic carbon, organic chelating agents and their decomposition products (on selected samples only), formate and oxalate.

For data to support source term evaluation:

- Radionuclides
- Toxic components

Other supporting data:

- Bulk enthalpy characteristics.

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5.0 DECISION BOUNDARIES

5.1 DETERMINATION OF WHEN CORE SAMPLES ARE REQUIRED

As discussed earlier, the Flammable Gas Safety Issue is concerned with the presence of flammable gas mixtures in the dome space of the waste tanks. There are two situations that must be addressed for this issue: (1) evaluation of the gas concentration in the dome space, and (2) estimation of the stored gas that could be released into the dome space. The first situation is being addressed by installation of gas monitoring system that will provide for continuous monitoring of hydrogen and periodic monitoring of other gases. At this point in time, engineering calculations must be performed to provide an estimate of the stored gas. Various models (Spore 1994) have been used to estimate the gas content of the waste. Not all of the stored gas is releasable, thus the evaluations have to account for the fraction that could be promptly released. The primary indicators of stored gas arise from analysis of waste surface level data and the axial temperature profile within the waste. Efforts are underway to upgrade the instruments for level and temperature measurement. Also, as mentioned previously, surface level response to barometric pressure variations is being studied as a measure of quantities of trapped gas.

Criteria can be set to determine if a hazardous situation exists. For the dome the standard industry approach is to use a gas concentration that is 25 percent of the LFL. This value is that recommended by the National Fire Protection Association (NFPA) and DOE Order 5480.4 requires that the NFPA guidelines be used for nuclear facilities. The specification (Sherwood 1995) for gas monitoring uses an action limit of 0.625 vol% for hydrogen. This value was chosen to account for the effect of other gases on the LFL of relative hydrogen.

Dealing with the stored gas must provide a limit that is consistent with that used for the dome space. Thus, the amount of stored gas that is considered to be releasable must be less than that amount when promptly mixed within the dome space yields a hydrogen concentration greater than 0.625 vol%. Thus, if the dome space never exceeds 0.625 percent and if the stored gas amount never exceeds the critical volume, then flammability concern is minimized. Core sampling is not needed and the tank only needs to be monitored, unless some tank trends indicate a need for analysis or core sampling is required to satisfy requirements of any final version of the Accelerated Safety Assessment (for example, to provide source terms for hazard assessment of a plume burn).

There is one variation on the stored gas that also needs to be addressed, namely that of a pressure pulse without ignition of the gas. The high-efficiency particulate air (HEPA) filters on the tanks have an operating limit of + 10 in. WG. If the pressure exceeds this value there is a chance that the filter seal will be breached and then there is an open pathway to the environment. Thus, the evaluation of stored gas must also consider the case of a pressure pulse that could burst the HEPA filters. This has been discussed in more detail in

Hopkins 1994. The criterion developed by Hopkins was to set the limit at 25 percent of the pressure that would cause a serious release to the environment. Again, if it is determined that such a situation does not exist, then core sampling is not needed. As this point, the logic for determining whether core sampling is needed is outlined in Figure 1.

The most important items in evaluating the nature of the waste as it affects the safety issue are the gas content and the physical properties (density, viscosity, solids, etc.). Equipment is being developed to perform in situ measurement of the gas bubbles and some physical properties (viscosity, yield strength) and to capture a waste sample while retaining all of the gas (free bubbles plus dissolved) for detailed analysis in the laboratory. Once these items have proven to be successful, then they would be used prior to waste sampling if any of the criteria are exceeded. After evaluation of the data, it may be determined that other chemical and physical data on the waste are needed and then core sampling would be conducted.

Studies are ongoing in several of the flammable gas concern areas. Outcomes of these studies can affect the basic data requirements for Flammable Gas Watch List tanks. Of these studies, those with the greatest possible impact on data requirements waste sampling needs are as follows:

- Plume burn analysis is determining the size of flammable gas release which can burst a HEPA filter upon ignition.
- Ammonia monitoring and in situ sampling will develop further data for a number of tanks. Research is continuing on ammonia and nitrous oxide accumulation mechanisms. Further study will more clearly determine likely bounds for ammonia and nitrous oxide releases and for their possible accumulation in single-shell tank salt-cake voids and depressions and tank dome volumes.
- Core sampling experiences have indicated possible accumulation of gases in pockets in 101-SY and 103-SY nonconvecting layers. Studies underway at PNL are directed toward better understanding of the physical limits of such accumulations and their effect on gas releases.

5.2 TANKS TO BE SAMPLED

The analysis discussed in Spore (1994) showed that the double-shell tanks 103-SY, 101-AW, 103-AN, 104-AN and 105-AN contain sufficient stored gas such that on a prompt release the hydrogen concentration would exceed the criterion given in Section 5.1. Requests for core sampling these tanks have been made and they have been included in the Baseline Sampling Schedule. Analyses are underway for the 19 single-shell tanks that are on the Flammable Gas Watch List. At this time no determination of the need for waste sampling has been made. Also, gas monitors are being installed on these tanks and will be operational

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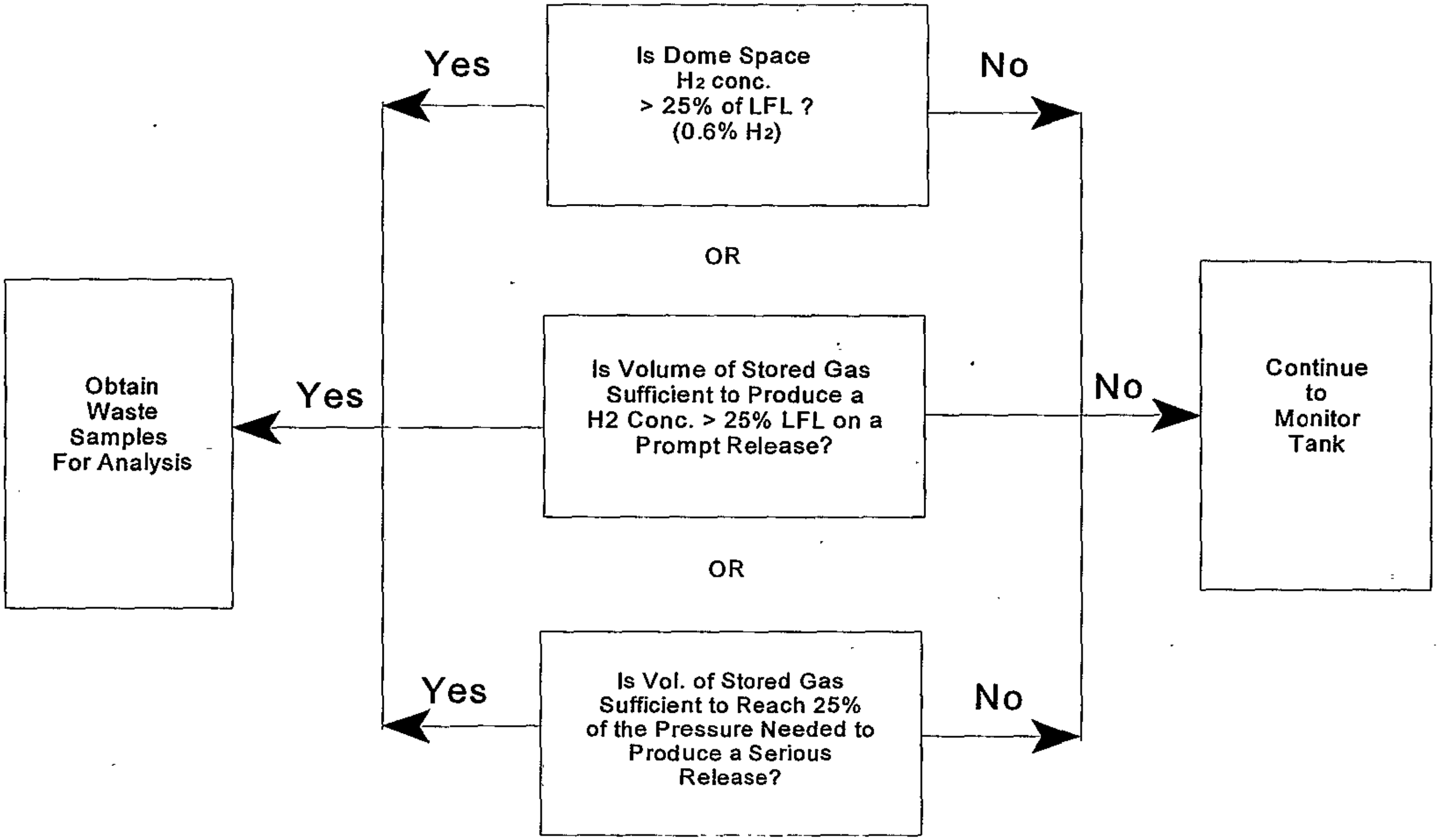


Figure 1. Decision Logic for Obtaining Core Samples.

by mid fiscal year 1995. Once the data have been obtained from the gas monitors and the waste behavior analyses are complete, then sufficient information will be available with respect to the criteria given in Section 5.1.

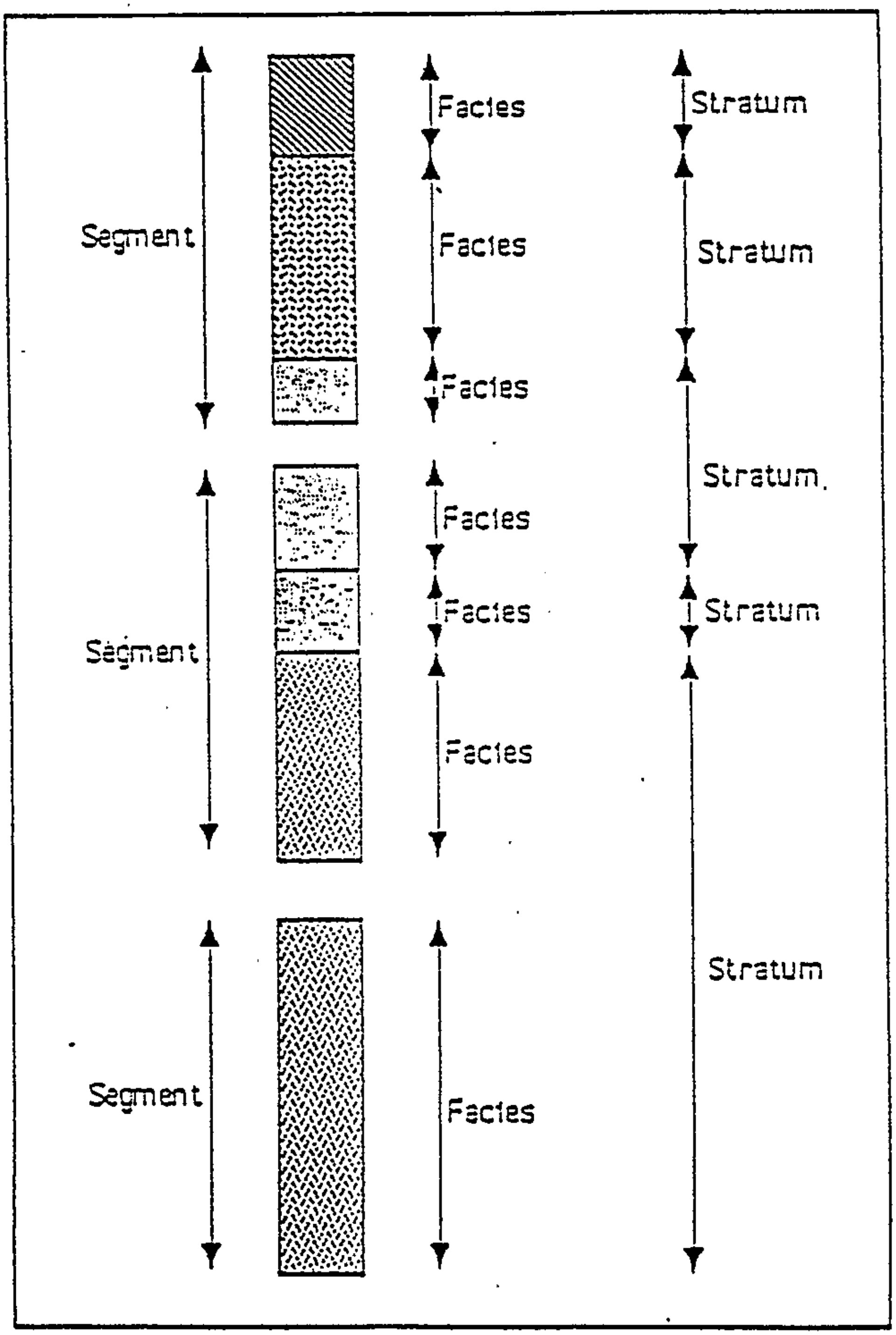
5.3 CORE SAMPLE REQUIREMENTS

Core samples are to be obtained for the entire depth of the tank. Experience with Tank 101-SY has shown that four layers may exist in the tank. The top of the waste may have a crust layer from a few inches to several feet in thickness. The very bottom of the tank has a sludge layer of a few feet. The majority of the tank is comprised of two major layers, a convective layer that is under the crust and a non-convective layer below the convective layer. In Tank 101-SY these two layers were each fairly well defined. However, the analysis plan must be able to take in account any distinct layer found from the core sampling of any specific tank, without over-reliance on paradigms developed from 101-SY.

A description of the layers that might be found in core samples is shown in Figure 2 (Jewett 1992). The core sampling is done by segments, each of which is about 47.5 cm (19 in.) in length. Two terms need to be defined, namely "facies" and "stratum." A facies is a region of waste, not longer than one segment, having a visually uniform appearance. One core segment may have several facies, but a facies is never larger than one segment. A stratum is generally assumed to represent a horizontal layer of waste in the tank. It may be as small as a facies or it may encompass several consecutive core segments of uniform appearance. The entire core sample from the tanks in question will range from 18 to 22 segments.

For the convective and non-convective regions composite samples will be made from the core segments that comprise each region. If facies or strata are found within each region, then samples must be retained for each facies and each stratum.

Figure 2. Segment-Facies-Stratum Relationship Diagram.



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6.0 DECISION RULES

There are no decision rules for waste samples at this time. The information is needed to provide basic information about the physical and chemical properties of the waste and to support work being done for mechanistic studies, safety analyses, and development of mitigation strategies. However, even though no decisions are to be made for the current work, it is possible to indicate what those decisions may be once the basic information is obtained.

Section 3.0 listed the four main questions that need to be answered. The first one dealt with the mechanism for gas generation. From current laboratory studies being conducted on simulated waste samples, it is known that the major factors influencing gas production are concentration of certain species, temperature, and radiation dose. Important chemical species are the organic chelating agents and their degradation products, aluminate, nitrite, hydroxide, transition metals, chloride and noble metals. So far 20 major organic species have been identified for 101-SY waste samples. These coupled with the inorganic species present a very complex situation. As the laboratory efforts develop the understanding of the mechanisms that generate hydrogen, nitrogen, nitrous oxide, ammonia and methane, it would be desirable to identify certain species or concentrations of these species such that a decision could be made as to what items would represent the limiting steps in the production of gas. Then, the core sampling efforts could be focused for these particular species, However, at this time, the first step is to get an understanding of what is in each tank and how these species play a role in the processes occurring in the waste. Successful deployment of the Retained Gas Sampler will aid greatly in this process; however this is pending final development of the sampler and related analytical procedures.

The next item given in Section 3.0 concerned the entrapment and release of the gases. Again, based on laboratory studies, it is believed that the major reason for gas retention is related to the physical properties. Analysis of waste samples from 101-SY showed that the viscosity was very high and that some segments of the waste actually exhibited a yield strength. In addition, the gas can be trapped because of the hydrostatic pressure. Knowledge of the waste density is needed for determining this pressure at any given depth. Experience with 101-SY waste material showed that the waste contains a large amount of small solid particles. The presence of these particles will greatly influence the physical properties, and the particles will also act as sites for gas bubbles.

The nature of retention is not completely understood. A number of potentially significant interactions with the particles, or aggregations, may exist, either singly or in combination. Studies of retention and release mechanisms are still ongoing. Details are not covered in this document. The retention of gas within the waste represents a greater problem than gas generation. Gas generation is not a problem if the gases are released from the waste and if the tank ventilation system can successfully remove them from the tank dome space. Retention of gases, as with tank 101-SY, can lead to large inventories of gas that when released, present a serious situation. Thus, a basic understanding of gas retention mechanisms may be the most critical item related to the safety issue. As this understanding is developed, it might be possible to specify a given value of solids content, viscosity, or some other property that would indicate that a certain action is needed. However, much work is still needed to develop this information.

The third question in Section 3.0 covered the situation for ensuring that future tank operations would not result in creating the flammability safety issue. It is envisioned that by gaining basic information about the chemical and physical properties of each of the tanks listed in Section 5.2 that it may be possible to relate this information to the observed tank behavior (i.e., changes in surface level, temperature, type of gases emitted, etc.). This then might show which properties or chemical species have a common link in the observed behavior. As a simple example, limiting densities may be set for evaporation of specific types of wastes or for mixing of specific waste concentrates.

Finally, Section 3.0 indicated that information was needed to evaluate dose consequences. Analysis for various radionuclides and toxic chemicals will provide the requisite information. Hazard analyses for the various tanks would then indicate the potential for any dose that would exceed established guidelines. Results from these evaluations might be used for establishing new work controls for the various tank activities.

7.0 CONSEQUENCES OF DECISION ERRORS

Since no decisions are to be made at this time for the data obtained on waste samples, there is no impact of decision errors. As an understanding is developed for the behavior of the tanks, decisions can be established and the DQO then will be updated. However, potential consequences for the items discussed in the previous section can be considered, but it should be pointed out that any discussions of decision errors at this time must be considered to be speculative. The complete spectrum of false-negative and false-positive consequences will not be considered; only examples of some will be given.

With respect to decisions that might be established for determination of which species are critical for gas generation, it is assumed that the decision would be directed at two situations, one for development of a mitigation method and the other for a process specification for future waste processing operations to ensure that flammable gases would not be generated in sufficient quantity to be of concern. In the case of mitigation, an incorrect identification of a particular species, or concentration of such a species, could lead to establishing the wrong process for removal of it from the waste. This would be a severe cost penalty and would still leave the safety issue unresolved. This could also be the case for a waste processing specification(this is the third question); the wrong parameter might be established and the waste might end up producing another flammable gas tank.

Decisions for gas retention might lead to development of a mitigation process. For instance, if the parameter were concerned with viscosity, a decision might be made to dilute the waste so as to reduce the viscosity. Possible consequences of having an error in the analysis, could then lead to excessive generation of additional waste, when, in fact, it would not be needed to mitigate the situation and on the other hand the dilution may not implemented when, in fact, it was needed. Decisions for dealing with the gas retention question might involve several key properties which may then need several related decisions. Consideration of the consequences would thus be an involved process. This can only be developed when all of the data have been analyzed and interpreted.

Consequences of an incorrect analysis for radionuclides could lead to overly restrictive work controls in one case and on the other hand an underestimate of the potential dose consequences would lead to an incorrect safety basis for the tanks.

These are only some examples of consequences that might develop for the results of sample analysis for decisions related to the questions given in Section 3.0. Again, as stated earlier, these will have to be developed after the basic understanding of the waste is developed and at that time the DQO will be revised accordingly.

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8.0 SAMPLING AND DESIGN OPTIONS

Current data gathering procedures covered under this DQO are for sampling the waste by either the rotary mode or push-mode core sampling or even with the "bottle-on-a-string" method for grab samples. However, it should be noted that the rotary mode core sampling system has not yet been qualified for use in potentially flammable atmospheres, but should be available in fiscal year 1995.

8.1 CORE ANALYSES

For the double-shell tanks, at least one complete core will be taken. Experience with 101-SY (Herting 1992a, 1992b) showed little variation for most analyses for the two cores. Needs for cores from the single-shell tanks will be determined as discussed earlier (Section 5.0). Planning for the taking of cores will be integrated at the characterization planing stage with needs of all other programs requiring core samples. Assumptions of homogeneity made for the double-shell tanks do not necessarily apply to the single-shell tanks; requirements for more than one core per tank will be determined in conjunction with the Tank Characterization Program.

The core segments will be examined during laboratory extrusion, following procedures developed for Tank 101-SY "Window E" cores (Jewett 1992). If visual examination reveals incomplete samples, the Flammable Gas Safety Program representative will decide upon options of retrieving another core from the tank. Also, if distinct stratification, as described in Section 5.0, is revealed, the Flammable Gas Safety Program will need to determine whether cores from other locations in the tank should be taken (to study inhomogeneity in tank contents). For each core, composites will be made up of discrete distinguishable strata.

Where appreciable amounts of drainable liquids are collected, the Flammable Gas Safety Program representative will determine appropriate testing and compositing to be performed with the samples of liquid collected. For guidance, Tank 101-SY is considered to contain four major strata: a bottom sludge layer, a non-convecting lower layer, a convecting middle layer, and a crust layer. The convecting layer is expected to be predominantly drainable liquid; if appreciable solids are found in this layer, they will be analyzed separately, with appropriate compositing determined by the Flammable Gas Safety Program. Laboratory analyses required on the composites (and on individual core segments where indicated) are presented in Table 2 for physical tests and Table 3 for chemical tests. The specific Tank Characterization Plan will provide detailed information for these laboratory tests.

Table 2. Core Physical Properties Data Requirements.

No.	Data name	Procedure type	Temperature °C	Desired Accur.	Desired Prec.	Reason for Analysis
1	Stratum identification, description	Visual observation of segments during extrusion	Ambient	NA	NA	Zone identification
2	Bulk density	Weigh and measure volume (volumetric flask, calibr. Centrifuge cone, or dimensions of solids)	Ambient	10%	10%	Buoyancy evaluations, mass balances
3	Viscosity	Bolin or Haake viscometer, cone and plate as required	40, 65, 90	10%[1]	LOE	Modeling input for pumping, mixing
4	Shear strength (on each segment, before mixing)	Vane test	40, 65, 90	10%[2]	LOE	Modeling input
5	Volume fraction of centrifuged solids	Centrifuged solids	Ambient and 60	LOE	LOE	Material balances, model input
6	Density, liquid fraction	Weight/volume measurement or digital density meter	Ambient	LOE	10%	Material balances, model input
7	Density, solid fraction	Calibr. Centrifuge cone	Ambient	LOE	LOE	Material balances, model input
8	Bulk enthalpy character.	Differential scanning calorimeter	20 - 450	LOE	LOE	Thermal reactivity
9	Solids settling rate	Visual measurement	40 and 60	LOE	LOE	Model input
10	Solubility in 2.5M NaOH	Volumetric, mass	40 and 90	LOE	10%	Dilution effects
11	Solubility in water	Volumetric, mass	40 and 90	LOE	10%	Dilution effects
12	Volatiles content*	Thermogravimetric analysis	20 - 450	LOE	10%	DSC interpretation, water

LOE = Level of effort
NOTE: Tests to be conducted on composite samples of crust, convecting layer, non-convecting layer, and sludge unless otherwise specified.
*As required for DSC interpretation, but required for any solid crust samples.
[1]Instrument to be checked for precision using newtonian fluid viscosity standard.
[2]Instrument to be checked for precision using bentonite test mixture.

Table 3. Core Chemical Data Requirements.

No.	Data name	Procedure type	Desired		Note	Reason for analysis
			Accur.	Prec.		
1	Total organic carbon (TOC)	Direct hot persulfate method	20%	20%		Reactivity
2	Formate and oxalate contents	Chromatographic method	TBD	15%	1	"Dead" organics
3	^{137}Cs,^{90}Sr,^{241}Am,^{239}Pu,^{238}Pu, ^{237}Np, ^{242}Cm, $^{243/244}Cm$, ^{99}Tc, ^{129}I, ^{60}Co, ^{154}Eu, TOTAL ALPHA, TOTAL BETA, (^{63}Ni, if PNL method is ready), ^{3}H (IN $^{3}H_2O$)	Appropriate γ, β, α counts, gamma energy analysis, with separation chemistry	20%	20%	2	Source term analysis for safety evaluation
4	Na,Al,Cr,Ca,Fe,K,Ni,Zn, Zr,Ba,Si,B,Bi	Inductively coupled plasma	15%	15%		Chemical definition
5	Total inorganic carbon (TIC)	Acidification of carbonate	15%	15%		Chemical definition
6	ANIONS: NO_3^-,NO_2^-,PO_4^{3-},SO_4^{2-}, Cl^-,F^-	Ion chromatography	20%	20%		Chemical definition
7	Hydroxide ion (OH^-)	Titration, pH	10%	10%		Chemical definition, corrosion
8	Water	Thermo gravimetric analysis	LOE	10%		Material balance
9	Cr(VI)	Spectrophotometric	20%	20%		Chemical definition
10	Total uranium	Laser fluorescence	20%	20%		Safety analysis

NOTE: (1) Expected accuracy to be determined with method development.
(2) Both water (acid, where required) digest and fusion methods to be used (with laboratory judgement).

GENERAL: Desired accuracy and precision (rpd) listed are upper limits expected for methods now in use, all limited to numbers above given detection limit; tests to be conducted on layer composites (as in table iii), unless otherwise specified. Detailed organic analysis will be done on a development basis for selected samples.

Maximum uncertainty bounds are presented as desired accuracy and precision in the tables. In general, these are bounds developed for expected relative percent difference for current laboratory analyses on well-mixed homogeneous samples without sample matrix interferences. Departures beyond these bounds may occur for tank samples. The required number of cores for single-shell tanks will need to be developed.

It is necessary to ensure that proper quality assurance requirements are used for the various procedures. This was established for the waste sample analyses performed for tank 101-SY. The same requirements should be used for the analyses described in this DQO. The requirements for duplicate, replicate, blank, spike, and blind analyses are given in Table 8-2 of Jewett 1992.

Core segment samples should be retained until deemed no longer required for (1) rechecking of analyses, or (2) future evaluations. Archived samples do undergo deterioration along with contamination from containers. Also, hot-cell space limitations preclude long term archiving of large numbers or volumes of samples. Surplus sample material shall be archived for at least one year after formal reporting of laboratory results, and disposal shall be executed only with approval of the Waste Tank Safety Program management (see Strong 1992).

8.2 USE OF HISTORICAL DATA

It is desirable to minimize the number of analyses to be conducted on core samples through the use of prior analyses conducted for the waste tanks. Such data must have been taken at a time as to be applicable to the safety issue. Table 4 provides a summary for the double tanks in question. For Tank 241-SY-103 the last major addition of waste occurred after the last chemical analysis. No analyses have been conducted since the tank started to exhibit gas release events, thus the full suite of analyses listed in Tables 2 and 3 must be conducted. Tank 241-AW-101 was sampled since the tank started to exhibit gas release events, thus some analyses do not need to be repeated. For the AN tanks, the last analyses were done as part of the evaporator campaign when the tanks received the last addition of waste. It may be possible to use some of these data. Selection of which data can be used from the historical information will be done at the time the Tank Characterization Plan is prepared.

Table 4. Use of Historical Data.

Tank	Date of last addition of waste	Date of last chemical analysis	Start of gas release events	Use historical data?
103-SY	1989	1986	1989	No
101-AW	1986	1990	1986	Yes
103-AN	1986	1987	1992	Maybe
104-AN	1985	1985	1986	Maybe
105-AN	1985	1985	1987	Maybe

References: Brager 1994, Reynolds 1994, Wilkins 1994.

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APPENDIX A

DATA QUALITY OBJECTIVES DEVELOPMENT PROCESS

The participants in the Data Quality Objectives (DQO) development process agreed initially that the following groups should be involved: Westinghouse Hanford Company (WHC) and Los Alamos National Laboratories (LANL) safety experts, WHC and Pacific Northwest Laboratory (PNL) computer modelers, PNL laboratory simulant researchers, test plan generators, WHC and PNL laboratory analytical scientists, and appropriate technical experts from WHC and PNL, with facilitation by PNL and Neptune and Company (Neptune).

Consistent with the Tank Waste Remediation System (TWRS) DQO Strategy (Babad et al. 1994) the DQO presented herein is generic (to the Flammable Gas Watch List tanks) in nature. Developing DQO for a generic problem required an adaptation of the DQO process. The DQO process guidance (EPA 1993) focuses on eliciting the input required to develop a statistical design for a specific data collection event in support of a specific decision. Generic DQO to support decisions for the flammable gas watch list tanks serve different functions, since the decisions are made in a process of logic based on a number of inputs. The DQO presented herein will be reviewed upon completion of each core sampling activity and will be updated accordingly. It is possible that in a number of instances insufficient data will be available to generate a statistical design satisfying the data quality objectives stated in this or other DQO documents. In these cases, a number of critical assumptions must be made, and data quality assessments must be performed to confirm data adequacy for decision making. Then the DQO document serves to guide the design in a qualitative sense during planning, and it can provide guidance for quantitative analysis of data adequacy when data are collected.

Data requirements for the Flammable Gas Watch List tanks were developed in a DQO process with outputs for each step of the process being elicited through a series of meetings. Meetings of WHC and PNL engineers, scientists, and statisticians were facilitated by experienced DQO representatives following the U.S. Environmental Protection Agency (EPA) guidance document (EPA 1993). The process was launched with an organizational meeting held by the Flammable Gas Tank Stabilization program manager, the PNL DQO coordinator, a representative from the Tank Waste Remediation System Characterization Program, and a senior level manager involved in this program. In this meeting, the major objectives of the DQO development task were discussed, and the technical experts and stakeholders who needed to be involved were identified. PNL subsequently organized a series of meeting locations and dates and invited each of the identified persons to attend. PNL provided DQO facilitators (Neptune) to assist the WHC program manager in conducting the meetings and documenting the outcomes in appropriate formats. Table A-1 summarizes attendance at the meetings so organized. In addition two separate meetings were held to brainstorm needs in modeling of tank waste behavior and in synthetic and actual waste laboratory studies. These two day-long meetings included scientists and engineers from WHC, PNL, and LANL involved in support work for the Flammable Gas Safety Program. Inputs from these two meetings (see Appendix B) were also used to derive data needs for the program.

Table A-1. Data Quality Objectives Planning Participants. (2 Sheets)

Participant	Role	Meeting dates					
		Nov 16	Dec 1	Jan 4	Jan 20	Feb 3	Apr 27
Jerry Johnson, WHC	Program Manager	X		X	X	X	X
Harry Babad, WHC	Technical experts		X				
Don Baker, WHC		X					
Tom Beaver		X					
Alan Brothers, PNL						X	
Joe Brothers, PNL		X		X	X	X	X
George Fox, Technology Applications						X	
Dave Hopkins, WHC				X			X
Rick Johnson, LANL							X
Dennis McCain, WHC							X
Norton McDuffie, WHC		X	X	X	X	X	X
Dan Reynolds, WHC			X	X	X	X	
Fred Riedel, WHC							X
Dave Sherwood, WHC							X
Dan Stepnewski, WHC					X	X	
Eric Straalsund, WHC				X			
Kathryn Tominey, PNL-WSD				X			
Dave Wooten, Technology Applications						X	
Patty Morant, WHC-HASM	Analytical Experts		X	X			X
Rudy Allemann, PNL				X			

Table A-1. Data Quality Objectives Planning Participants. (2 Sheets)

Participant	Role	Meeting dates					
Catherine Anderson, PNL	Analytical Experts (continued)			X		X	X
Brent Pulsipher, PNL							X
Randall Ryti, Neptune and Co.	Facilitator/ Statistician		X			X	
John McCann, Neptune and Co.	DQO Process Facilitators			X		X	
Dan Michael, Neptune and Co.			X		X		X
Dean Neptune, Neptune and Co.		X	X	X	X		
Jerry Scott, PNL-Prog. Off.	DQO Logistical Support		X				
Paul Turner, PNL-Prog. Off.				X			
Megan Lerchen, WDOEcol	Stakeholders	X					
Gary Rosenwald, DOE-RL		X	X	X		X	
Milt Campbell, Mactec	DOE DQO Oversight						X
Larry Jackson, Mactec				X			
Ken Redus, Mactec			X				
David Schlick, Mactec							X
Steve Krogsrud, WHC	Safety						X
Mohammad Islam, WHC							X

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APPENDIX B

SUPPLEMENTAL MEETINGS TO SUPPORT DEVELOPMENT OF THE DATA QUALITY OBJECTIVES

I. MEETING ON CHEMICAL MECHANISMS

A meeting was held on November 23, 1993 to evaluate the work being done to determine the mechanisms responsible for gas generation and retention. A historical review was given for the work conducted at Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL), Georgia Institute of Technology, and Argonne National Laboratories to determine the nature of gas generation in synthetic and tank waste samples. Discussions were held as to what type of tests should be done to determine gas retention mechanisms. The effects of gas solubility also needed to be addressed as well as the effect of radiation on the stability of the various gaseous species. The final item discussed at this meeting concerned the type of analyses that needed to be performed on the core samples. In general, the attendees felt that the same analyses that were conducted for Tank 101-SY would be needed for the other double-shell tanks that are on the Flammable Gas Watch List.

The following list is a summary of the requested items:

- The major anions and cations
- The primary organics that were in the feed material
- The organic products in the waste, including oxalate and formate.
- TOC
- DSC/TGA
- Accountability for C, H, and N.
- % water
- Hydroxide
- Ammonia
- Noble metals
- Polarized Light Microscopy
- % solids
- Physical properties (density, viscosity, yield strength)
- Radionuclides
- Gas content of the waste and gas composition
- Knowledge of surfactants.

The following people attended the meeting:

H. Babad, D. L. Herting, C. Delegard, J. C. Person, D. A. Reynolds, S. A. Bryan, D. D. Stepnewski, G. L. Fox, R. J. Van Vleet, L. R. Pederson,

G. W. Rosenwald, M. Campbell, N. G. McDuffie, G. D. Johnson

II. MEETING ON MODELING ACTIVITIES

A meeting was held on December 16, 1993 to review the work being done on thermal, gas flow, combustion and waste modeling. The data needs for each type of modeling work are listed below.

a) Thermal Modeling

- Thermal conductivity (may be able to get from synthetic waste)
- Heat Capacity (may be able to get from synthetic waste)
- Density of waste
- Volumetric distribution of heat sources
- Solubility of various species
- Vapor pressure and density of vapor
- Soil thermal conductivity
- System operating parameters
    - Flow rates for dome and annulus
    - Air temperature for dome and annulus
    - Relative humidity
    - Waste temperature
    - Structural temperatures
    - Ventilation system configuration

b) Gas Flow Modeling

- System flow rates
- System configuration
- Psychometric data
- Vapor pressure data
- Gas composition

c) Waste Behavior Modeling

- Distribution of solids in the waste
- Gas content of waste and gas composition
- Distribution of gas in waste
- Viscosity
- Rheogram
- Yield Strength
- Density

- Particle size of solids
- Solubility of gases and solids
- Mechanism for gas retention and release

d) Gas Burn Modeling

- Properties of Crust
    - DSC
    - TGA
    - Adiabatic calorimetry
    - % water
    - Radionuclides
- Gas composition

The following people attended the meeting;

WHC: R. Van Vleet, D. Reynolds, W. Cowley, D. Stepnewski, G. Fox, W. Kencht, K. Sathyanarayana, T. McCall, F. Heard, S. Wood, T. Beaver, N. McDuffie, D. Hopkins, G. Johnson, B. Vonderfecht, R. Graves

PNL: C. Stewart, D. Anderson, Z. Antoniak, D. Trent, T. Michener, R. Allemann, L. Schienbein

LANL: K. Pasamehmetoglu, J. Edwards, B. Lin, J. Spore, R. Nelson

RL: G. Rosenwald.

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